Synthesis of High Molecular Weight Nylon 6 by Anionic Polymerization of ε-Caprolactam. Mechanism and Kinetics

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ABSTRACT: Studies on the mechanism and kinetics of the anionic polymerization of ε-caprolactam were carried out by observing the kinetic data. The kinetic data were obtained as the functions of the concentrations of the catalyst and chain initiator. The rate equation of the polymerization was derived as follows, $-d[M]/dt = k[I][C]$ ($[C] \leq 1.5 \times [I]$) and $-d[M]/dt = k'[I]^2$ ($[C] > 1.5 \times [I]$). Here, [M], [I], and [C] are the concentrations of monomer, chain initiator, and catalyst, respectively. This suggests that the reaction between lactam-anion and polymer chain end (acyl-lactam) is the rate-determining step of the polymerization. The intermediate route of the rate-determining reaction is likely the pathway where the protonation occurs on the oxygen atom (at the initial stage of the reaction) and ring-opening follows. The values of apparent activation energy for the polymerization were $19.0\,\mathrm{kcal\,mol^{-1}}$ ($[C] \leq 1.5 \times [I]$) and $20.7\,\mathrm{kcal\,mol^{-1}}$ ($[C] > 1.5 \times [I]$), respectively.

KEY WORDS   Kinetics / Mechanism / High Molecular Weight / Nylon 6 / Anionic Polymerization / ε-Caprolactam / Schlenk Equilibrium /

The anionic polymerization of ε-caprolactam has been extensively investigated because of the high yield and high rate of the polymerization.[1-4] Many studies on mechanism[5-15] and kinetics[16-27] of the anionic polymerization of ε-caprolactam have been carried out. The fundamental major reaction mechanisms of the polymerization were clarified by Sebenda et al.[5,6] and Sekiguchi et al.[8] who found the rate-determining step of the polymerization to be the reaction of lactam-anion with acyl-lactam. This mechanism may be acceptable except the part of the formation of the intermediates. It is difficult to detect intermediates of the reaction, so that some intermediate routes are proposed[7-9,12] and a new activating mechanism was recently shown using $NaAlH_2(OR)_2$ as the catalyst.[13,14] Various kinetic equations of the polymerization have been reported.[16-27] There is, however, no consistency with the kinetic data. Most experimental results are not in agreement with the kinetic equation based on the rate-determining step of the polymerization shown by Sebenda et al.[5,6] The structures of catalyst and chain initiator influence the kinetics, and especially the influence of the side reactions is large.[28]

Our preceding systematic studies were carried out directed on high molecular weight nylon 6 and the stable high-molecular weight polymer (the intrinsic viscosity, $[\eta] = 11.2\,\mathrm{dl\,g^{-1}}$; the weight average molecular weight, $M_w = 9.5 \times 10^5$) was obtained by controlling water content in monomer and concentration of the catalyst and chain initiator.[29,30] This paper deals with the mechanism and kinetics of the anionic polymerization of ε-caprolactam, which is close to ideal polymerization under isothermal conditions. This kinetic study was carried out by observing the polymerization rate obtained as a function of the concentration of the catalyst and chain initiator.

EXPERIMENTAL

Materials

Industrial fiber grade ε-caprolactam as monomer, ethyl magnesium bromide (EtMgBr; Aldrich Chemical Co.,

Inc.) as catalyst in $1.0\,\mathrm{mol\,l^{-1}}$ tetrahydrofuran solution and N-acetyl-ε-caprolactam (Ac-CL; Tokyo Chemical Industry Co., Ltd.) as monofunctional chain initiator were used for the polymerization. Other all chemicals were of reagent grade and used without further purification.

Polymerization

Water in ε-caprolactam was removed to less than 0.013 mol% by bubbling dry argon gas for 5 hours in a three-neck flask at 120°C. Water content was measured by Karl Fischer auto titration equipment (Hiranuma Industrial Co., AQV-5S). The chain initiator was injected into ε-caprolactam with controlled water content. The mixture of monomer and initiator was poured into a glass tube (inside diameter 20 mm, volume 20 ml) beforehand dried by heating above 100°C under 10 Pa of vacuum. The catalyst (EtMgBr) solution was injected into the tube by a syringe, and the tube was sealed after unnecessary solvent was evaporated at 10 Pa. Polymerization was carried out with shaking in an oil bath at 130—190°C (thermostated at ± 1.0°C) on the isothermal condition.

Termination of polymerization was carried out by quenching to dry ice/methanol temperature (−73°C). The product was shaved with a boring machine and analyzed. Monomer and oligomer in the polymer were extracted by boiling water in an ampoule for 5 hours. The monomer content in the extract was measured by liquid chromatography (column, Waters C18 Purecil; mobile phase, methanol/water = 65/35), and conversion was calculated from change in monomer content before and after polymerization.[29]

RESULTS

Influence of Catalyst Concentration on Kinetics

Figure 1 shows time–conversion plots for several concentrations of the catalyst, where the concentration of the chain initiator is 0.03 mol% and temperature is 150°C. A linear relationship between the reaction time
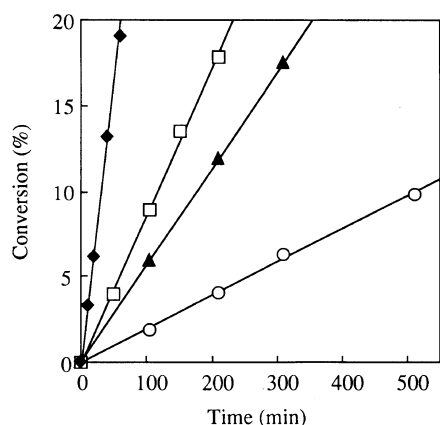
Figure 1. Time–conversion plots at several concentrations of catalyst and 0.03 mol% chain initiator at 150°C: (◆) catalyst concentration is 0.1 mol%; (□) 0.03 mol%; (▲) 0.02 mol%; (○) 0.01 mol%.
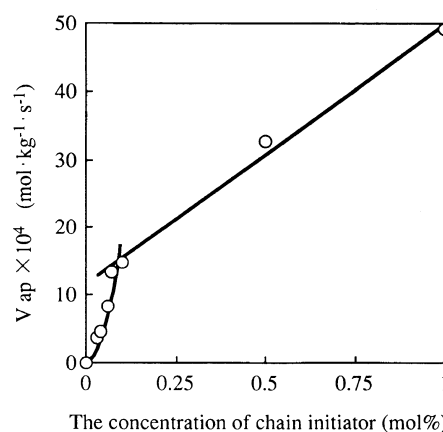

Figure 3. Relation between V_{ap} and concentration of chain initiator at 0.1 mol% catalyst at 150°C.
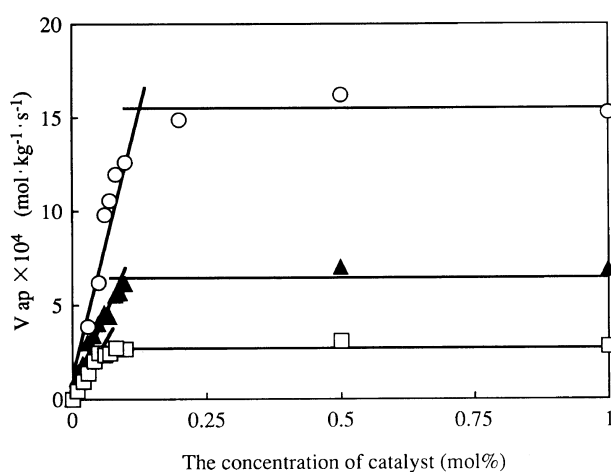

Figure 2. Relation between V_{ap} and concentration of catalyst at the concentration of the chain initiator: (○) 0.1 mol%; (▲) 0.05 mol%; (□) 0.03 mol% at 150°C.
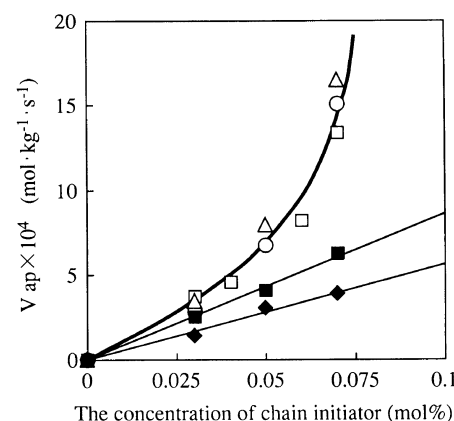

Figure 4. Relation between V_{ap} and concentration of chain initiator at the concentration of the catalyst: (○) 1.0 mol%; (△) 0.5 mol%; (□) 0.1 mol%; (■) 0.05 mol%; (◆) 0.03 mol% at 150°C.

and monomer conversion (up to 20 percent; 1.77 mol kg^{-1}) was obtained for all polymerizations. The apparent rate of the polymerization (V_{ap}) was determined from the slop of the plots. Figure 2 shows the relations between V_{ap} and the concentrations of catalyst at three concentrations of the chain initiator (0.03, 0.05, and 0.10 mol% of chain initiator, respectively) at 150°C. V_{ap} increases linearly with concentration of catalyst at the low catalyst concentration region. V_{ap} becomes constant at the region where the concentration of the catalyst is higher. The catalyst concentrations at the cross points were calculated by linear regression analysis as 0.14 mol% (0.10 mol% of chain initiator), 0.077 mol% (0.05 mol% of chain initiator), and 0.049 mol% (0.03 mol% of chain initiator), respectively. The ratios of the catalyst concentration to the chain initiator concentration ($\equiv [C]/[I]$) are 1.40, 1.54, and 1.63, respectively. V_{ap} reveals specific change at the region where the ratio of $[C]/[I]$ is approximately 1.5, this being the average of the above three. A set of the approximate linear equations was derived as follows;

$$V_{ap} = A[C] \quad [C] \leq 1.5 \times [I] \tag{1}$$

$$V_{ap} = B \quad [C] > 1.5 \times [I] \tag{2}$$

A and B are constants.

Influence of Chain Initiator Concentration on Kinetics

To clarify the influence of the concentration of the chain initiator on the rate of polymerization, V_{ap} was observed changing the chain initiator concentration. Figure 3 shows the relation between V_{ap} and the concentration of the chain initiator at the catalyst concentration 0.1 mol% and temperature 150°C. V_{ap} increases with concentration of the chain initiator. A linear relation is observed at the high chain initiator concentration region. The V_{ap} data against the concentration of chain initiator at various concentrations of catalyst are shown in Figure 4. Linear relations are obtained in the case of the low concentration of the catalyst (less than 0.05 mol%) in the region where the chain initiator concentration is less than 0.1 mol%. The non-linear relation data in Figure 4 are re-plotted in the form of $\log(V_{ap})$ vs. $\log[I]$ and shown in Figure 5. These data follow a straight line with a slop $=1.93$ (obtained by the linear regression analysis; approximately equal to 2). From this result, the non-linear curve in Figure 3 is approximately a quadratic equation. The chain initiator concentration at the cross point was calculated by linear regression analysis and the curve fitting to the quadratic equation as 0.069 mol%. The ratio of $[C]/[I]$ is 1.45 (approximately equal to 1.5). According to the results, a set of the approximate equations was derived as follows;
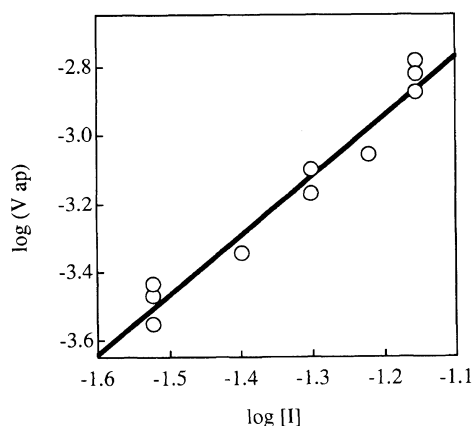
$$V_{ap} = A'[I] \quad [C] \leq 1.5 \times [I] \tag{3}$$

Figure 5. Log(V_{ap}) vs. log(concentration of chain initiator) in the area where the concentration of catalyst is greater than 1.5 times that of the chain initiator.
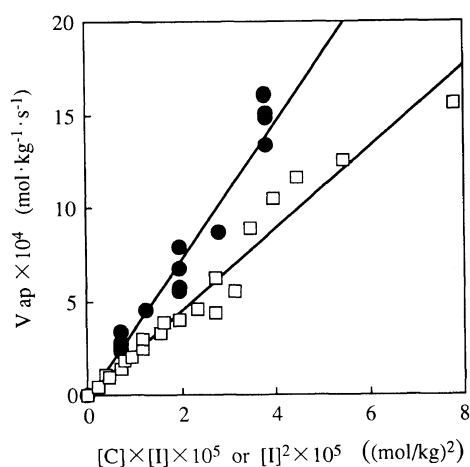

Figure 6. Relation of V_{ap} vs. [I] × [C] ($\square$, where [C] $\leq$ 1.5 × [I]) and V_{ap} vs. [I]^2 ($\bullet$, where [C] > 1.5 × [I]).

$$V_{ap} = B'[I]^2 \quad [C] > 1.5 \times [I] \tag{4}$$

A' and B' are constants.

Kinetic Equations

The kinetics of the anionic polymerization are dependent on the relation of the concentration of the catalyst and chain initiator. Equation 5 was derived from eq 1 and 3, and eq 6 was derived from eq 2 and 4.

$$V_{ap} = k[I][C] \quad [C] \leq 1.5 \times [I] \tag{5}$$

$$V_{ap} = k'[I]^2 \quad [C] > 1.5 \times [I] \tag{6}$$

k and k' are rate constants.

To evaluate the rate constants of eq 5 and 6, the plots of V_{ap} versus [I][C] and [I]^2 were carried out and shown in Figure 6. An approximately linear relationship exists for V_{ap} vs. [I][C] and V_{ap} vs. [I]^2, and k of eq 5 and k' of eq 6 were obtained from linear regression analysis.

$$k = 21.9 \ (Kg\,mol^{-1}\,s^{-1}) \quad [C] \leq 1.5 \times [I]$$

$$k' = 36.9 \ (Kg\,mol^{-1}\,s^{-1}) \quad [C] > 1.5 \times [I]$$

Figure 7 shows Arrhenius plot of log k vs. $1/T$ and log k' vs. $1/T$, where k and k' are the rate constants of the polymerization determined by eq 5 and 6, and T is polymerization temperature changed from 403 to 463 K
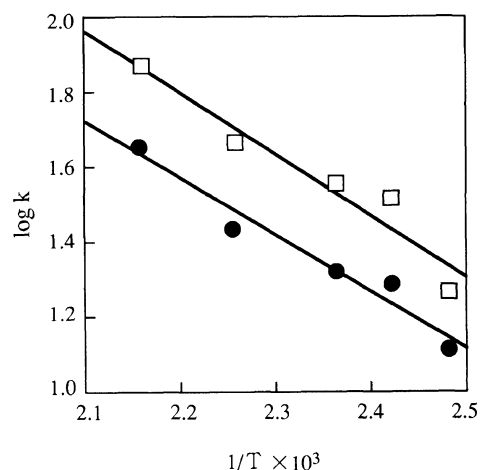
Figure 7. Arrhenius plots of reciprocal of time vs. log-rate constant ($\bullet$, k; $\square$, k') of polymerization.

(130 to 190°C).

$$\log k = -E_a/(2.303RT) + \log X \tag{7}$$

E_a is the activation energy, R gas constant and X a constant. The activation energy for the polymerization was evaluated as 19.0 kcal mol^{-1} ([C] $\leq$ 1.5 × [I]) and 20.7 kcal mol^{-1} ([C] > 1.5 × [I]), respectively by linear regression analysis.

DISCUSSION

Kinetic Equations

The mechanism of the anionic polymerization of ε-caprolactam was clarified by Sebenda et al.[5,6] and Sekiguchi et al.[8] as shown in Table I. They clarified that the rate-determining step of the polymerization was the reaction of lactam-anion with acyl-lactam (eq ii in Table I). Table II gathers the results of kinetic studies so far reported in the literature about the anionic polymerization of α-pyrrolidone[31,32] and ε-caprolactam.[16,19,21,27] These two lactams polymerize by the same mechanism and, therefore, they should obey the same kinetics. Equation 8 in Table II is considered to be the ideal equation, because it is based on the assumption that eq ii in Table I is the rate-determining step of the unit growth reaction. The two equations reported for α-pyrrolidone polymerization (eq 13 and 14 in Table II) are identical to the ideal equation, whereas no ε-caprolactam polymerization is not identical to the ideal equation. Our experimental results agreed with the ideal rate equation (eq 8 in Table II) in the case [C] $\leq$ 1.5 × [I]. The activation energy is a little higher than others in Table II. For [C] > 1.5 × [I], we considered as follows. The concentration of the essentially active catalyst is considered to be 1.5 times the concentration of the chain initiator in the case of [C] > 1.5 × [I], therefore, the following equation may be assumed.

$$[C]^* = 1.5 \times [I] \tag{14}$$

$[C]^*$ is the concentration of the active catalyst. If eq 14 is partially substituted into eq 6, then it is possible to obtain,

$$V_{ap}^* = 24.6 \times [I][C]^* \tag{15}$$

Table I. Reaction mechanisms of the anionic polymerization of ε-caprolactam[17,18,20]
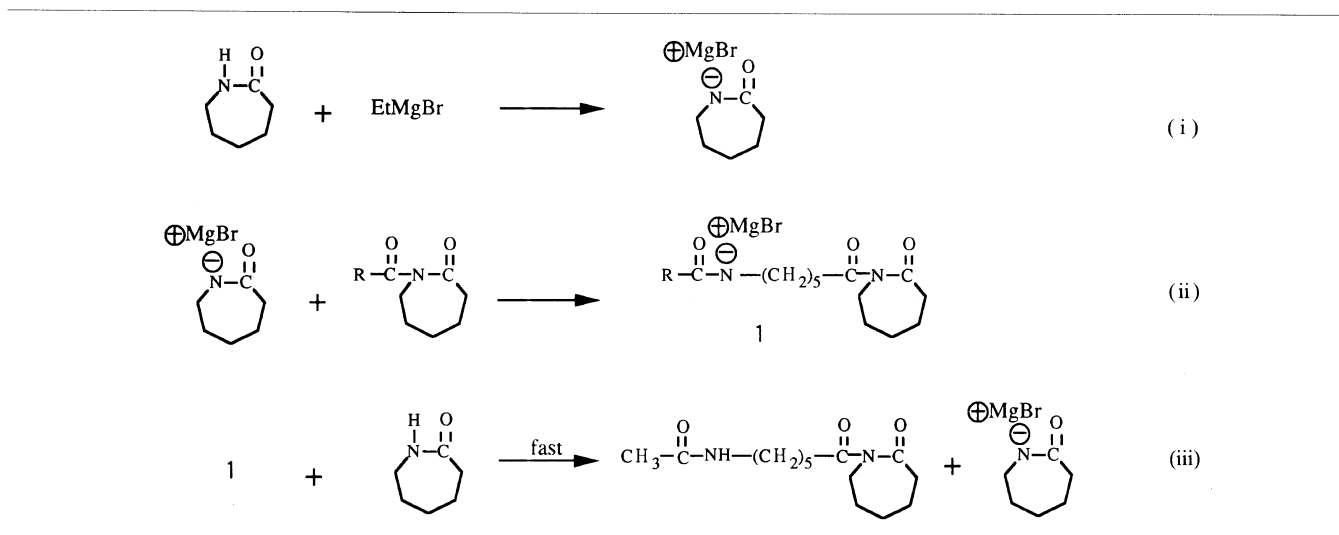
Table II. List of published kinetic studies

Authors	Rate equation, $-\dfrac{d[M]}{dt}$	$E_a/\text{kcal mol}^{-1}$	Eq. no.
Ideal	$k[I][C]$		(8)
Sittler and Sebenda (1968)[a]	$k \cdot K^{0.5}[I][C]^{0.5}$	17.5	(9)
Rigo et al. (1975)[b]	$K([M]-[Me])[I]_0[C]_0$	16.1	(10)
Greenley et al. (1969)[c]	$K_p[M][I]_0[C]_0{}^{0.5} - K_d[C]_0{}^{0.5}\{[M]-[M]^2\}$	12.6	(11)
Bolgov et al. (1981)[d]	$K\dfrac{[M][I]_0[C]_0}{[M]_0}\left\{1+\dfrac{m([M]_0-[M])}{[M]_0([I]_0[C]_0)^{0.5}}\right\}$	17.1	(12)
Barzakay et al. (1966)[e]	$k[I][C]$	—	(13)
Sekiguchi (1960)[f]	$k[I][C]$	—	(14)

[a] Catalyst, sodium-ε-caprolactam; chain initiator, N,N,N',N'-tetraacetyl hexamethylenediamine.[16] [b] Catalyst, sodium-ε-caprolactam; chain initiator, hexamethylene diisocyanate.[19] [c] Catalyst, ethyl magnesium bromide etc.; chain initiator, N-acetyl-ε-caprolactam etc.[27] [d] Catalyst, sodium-ε-caprolactam; chain initiator, N-acetyl-ε-caprolactam etc.[21] [e] Momomer, α-pyrrolidone; catalyst, magnesium bromide-α-pyrrolidone; chain initiator, N-acetyl-α-pyrrolidone. The equation was only applied to dimeric initiator reaction.[31] [f] Momomer, α-pyrrolidone; catalyst, sodium-α-pyrrolidone; chain initiator, N-acetyl-α-pyrrolidone.[32]

Since eq 15 is in almost agreement with eq 5 ($k=21.9$), the rate equation of the anionic polymerization may be eq 16 at $[C]\le 1.5 \times [I]$ and $[C] > 1.5 \times [I]$.
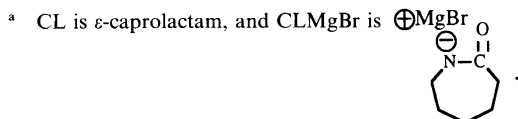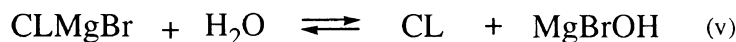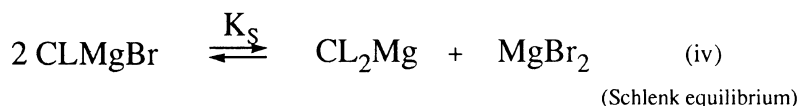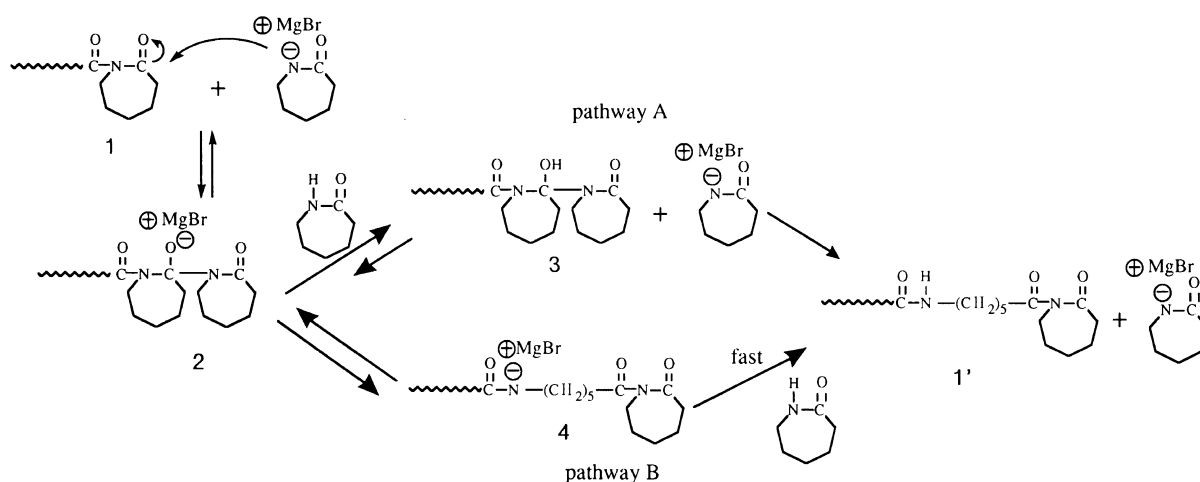
$$-d[M]/dt = k[I][C] \tag{16}$$

Here, $[M]$ is the concentration of the monomer. It becomes clear that our results of the anionic polymerization are compatible with the rate equation based on eq ii in Table I. In the preceding kinetic studies,[16,19,21,27] such a simple relationship as eq 16 (eq 8 in Table II) was not obtained as shown in Table II. This means that the mechanism of eq ii in Table I is the rate determining step and the side reactions such as the termination of polymer-chain-end (acyl-lactam) by water are very little in the polymerization (In this study, water content was controlled less than 0.013 mol%). This is the reason why we can synthesize the high molecular weight polymer (the intrinsic viscosity, $[\eta]=11.2\,\text{dl g}^{-1}$; the weight average molecular weight, $M_w = 9.5 \times 10^5$).[29]

The constant of eq 14 should be 1.0. The reason why the constant is 1.5 may be due to the presence of the inactive catalyst. Two inactivation reactions of the catalyst as the side reaction are shown in Table III.[6,26,33] Equation iv in Table III is called the "Schlenk equilib-

rium", a typical side reaction of the Grignard reagent. The equilibrium constant K_s of general Grignard reagent is ordinarily 1—500,[34] and the quantity of the inactive catalyst is not negligible. Therefore, in the presence of Schlenk equilibrium, larger amount than 1.5 times ideal quantity of catalyst is necessary to the polymerization.

Intermediate Mechanism

Our experimental results prove that eq ii in Table I is the rate-determining step in the polymerization.[16,17] There were two proposals for the intermediates route of this reaction such as the pathway (A; $2 \leftrightarrow 3 \leftrightarrow 1'$)[8,9] and (B; $2 \leftrightarrow 4 \leftrightarrow 1'$)[7] in Table IV. Our results support pathway (A) as the intermediate route, where the protonation occurs on the oxygen atom (at the initial stage of the reaction) and then ring-opening follows. This is explained by considering the formation of the lactam-anion as follows. That the polymerization rate increases with the concentration of the chain initiator without upper limit is elucidated on the basis of the formation of the lactam-anion. The lactam-anion is formed at the reaction $2 \leftrightarrow 3$ on pathway (A), while it is also formed at the reaction $4 \leftrightarrow 1'$ on pathway (B). The reaction rate of the polymerization does not increase with the concentration of

Table III. Side reactions of catalyst[6,27,32,33]

$$2\,CLMgBr \xrightleftharpoons[]{K_S} CL_2Mg + MgBr_2 \qquad (iv)$$

(Schlenk equilibrium)

$$CLMgBr + H_2O \rightleftharpoons CL + MgBrOH \qquad (v)$$

[a] CL is ε-caprolactam, and CLMgBr is

Table IV. Intermediate route of the rate-determining reaction[7,9,16]

pathway A

pathway B

chain initiator without upper limit on pathway (B), since the lactam-anion necessary to proceed the polymerization is formed at the last step in the pathway.

Assuming that intermediate route in the case of $[C] \le 1.5 \times [I]$ is pathway (A), the equilibrium of the reaction $1 \leftrightarrow 3$ is not reached and the reaction $1 \leftrightarrow 2$ is the rate-determining step because the concentration of the lactam-anion is not enough. The reaction rate of the polymerization is proportional to the concentrations of the catalyst and chain initiator. When $[C] > 1.5 \times [I]$, the concentration of the lactam-anion is enough, the equilibrium of the reaction $1 \leftrightarrow 3$ is established and the reaction $3 \leftrightarrow 1'$ is the rate-determining step. The reaction $3 \leftrightarrow 1'$ is monomolecular, so it is considered that the reaction rate depends on the concentration of 3 ($[3] = [2] = K_1[I][C]$, and K_1 is the equilibrium constant of the reaction $1 \leftrightarrow 2$). Consequently, the reaction rate in this case is also proportional to the concentrations of the chain initiator and catalyst. Pathway (A) explains the experimental results very well.

CONCLUSIONS

With respect to the mechanism and kinetics of the anionic polymerization of ε-caprolactam with controlled water content, the followings were clarified: (1) The rate equation of the polymerization is shown to be

$-d[M]/dt = K[I][C]$ ($[C] \le 1.5 \times [I]$) and $-d[M]/dt = k'[I]^2$ ($[C] > 1.5 \times [I]$). $[M]$, $[I]$, and $[C]$ are the concentrations of monomer, chain initiator, and catalyst. These results are compatible with the simple rate equation based on the elemental reaction. (2) The values of apparent activation energy for the polymerization are $19.0 \, kcal\,mol^{-1}$ ($[C] \le 1.5 \times [I]$) and $20.7 \, kcal\,mol^{-1}$ ($[C] > 1.5 \times [I]$), respectively. The apparent activation energy for the polymerization is $20.7 \, kcal\,mol^{-1}$. (3) The rate-determining step of the polymerization is the reaction of the lactam-anion with acyl-lactam. The intermediate route in the reaction may be pathway/where the protonation occurs on the oxygen atom (at the initial stage of the reaction) and ring-opening follows.

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